Asia-Pacific Journal of Science and Technology :Volume: 26 .Issue :02. Article ID :.APST-26-02-18. Research Article

APST

Asia-Pacific Journal of Science and Technology

https//:www.tci-thaijo.org/index.php/APST/index

Published by the Research and Graduate Studies,
Khon Kaen University, Thailand

A top-down approach to preparation of H-Y zeolite nanoparticles

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Received 18 December 2020
Revised 30 March 2021
Accepted 1 April 2021

Abstract

Zeolite is an aluminosilicate material formed of 3D pores containing channels and cages of many different topologies, including sodalite (SOD) and faujasite (FAU) framework types. H-Y zeolites (FAU-type framework) are widely used as active components of catalysts for petroleum refining and petrochemical processes. The archetypal H-Y zeolites used in the industry have a large particle-size morphology and there has recently been a growing interest in using zeolite nanoparticles (NPs) due to their desirable characteristics. Ball milling (BM) offers an easy, fast, and environmentally friendly way to produce zeolite NPs from commercially available zeolite microparticles. Although BM effectively reduces the particle size of zeolite, it is often accompanied by a reduction in crystallinity. In this report, a study was conducted with the intention of improving the crystallinity of H-Y zeolite NPs after BM. Alkaline leaching using NaOH was found to further reduce the particle size of the NPs, leading to an amorphous phase. In contrast, recrystallization in a dilute aluminosilicate solution transformed the H-Y zeolite from a FAU-type framework to the SOD type.

Keywords: H-Y zeolite, Ball milling, Alkaline leaching, Recrystallization, Nanoparticles

1. Introduction

Zeolites are microporous crystalline aluminosilicate materials with a large surface area, and high ion exchange capacity and catalytic activity due to the presence of basic/acidic active sites. Zeolites were first reported in 1756 as minerals that produced an excessive amount of steam upon heating. Natural zeolites are commonly found in sedimentary rock [1], but the first synthetic zeolite, mordenite-type zeolite, was reported in 1948 [2]. Silica and alumina tetrahedra are the primary building units of zeolites. Corner sharing of these tetrahedra produces secondary building units that later form composite building units (CBUs), with further arrangements of CBUs producing porous materials containing channels or cages of different topologies. As of 2020, 253 framework type codes have been designated by the Structure Commission of the International Zeolite Association [3]. Some well-known framework types include sodalite (SOD), Linde Type A (LTA), and faujasite (FAU). These three framework types share similar CBUs, namely *sod*. The *sod* CBUs have a truncated octahedron shape containing eight six-membered ring (6R) and six four-membered ring (4R) windows. Upon arrangement of the *sod* CBUs, if only *sod* CBUs are involved and are stacked upon one another at the 4R windows, the SOD framework type is formed. If the arrangement involves a formation of a double 4R, with CBUs in the gap between each 4R window of the *sod* CBUs, the LTA framework type is formed. If the *sod* CBUs are stacked upon one another at the 6R windows through the formation of a double 6R (*d6r*), a FAU-type zeolite is formed. A comparison of these three related zeolite framework types is illustrated in Figure 1[3].

Zeolites with an SOD framework are used as semiconductors, matrices for pigments, adsorbents for hydrogen storage and separation, and catalyst supports [4]. In contrast, zeolites with an FAU framework are

used extensively in industry as materials for purification and separation, as well as being catalysts. Some examples of FAU-type zeolites are Na-X, Li-X, and H-Y. Whereas Na-A (LTA-type framework) zeolites are well-known as molecular sieves for adsorption and separation, H-Y zeolites are widely used as active components of catalysts for fluid catalytic cracking and hydrocracking processes in petroleum refining. In fact, H-Y zeolites are the second-most-produced synthetic zeolites in the world; zeolite A is the most-produced synthetic zeolite and is widely used as an ion exchange builder in home detergent [5].

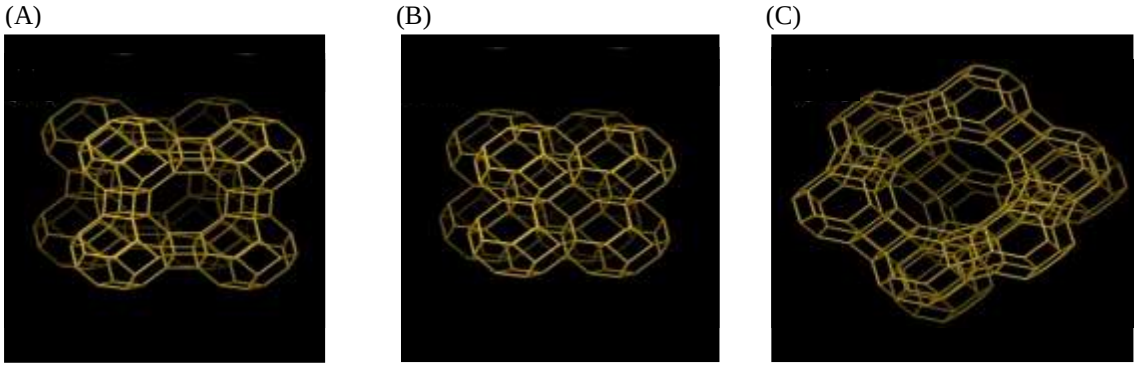

Figure 1 Cartoon image comparing the topology differences among three types of zeolite frameworks: (A) Linde Type A, (B) sodalite, and (C) faujasite (images adapted and modified from [3])

The H-Y zeolites used in industry typically have a large particle size (D50 = 550 nm). The zeolite particles are combined with additives and binder, and then shaped into extrudates or granules prior to loading into the reactor. Recently, there has been a growing interest in using zeolite nanoparticles (NPs), due to their more exposed active sites, and low reactant and product diffusion limitations, as compared to zeolite microparticles (MPs). These characteristics of NPs offer better reactant conversion, product selectivity, and catalyst stability. A residue fluid catalytic cracking (RFCC) catalyst prepared using Na-Y NPs was reported to show higher catalytic activity in comparison to micron-sized Na-Y particles [6]. Furthermore, the formation of undesired coke and heavy cycle oil products was lower when the Na-Y NP RFCC catalyst was used. The large external surface area provided by the NPs provided better access for the conversion of heavy hydrocarbon molecules, as compared to the Na-Y MPs. Despite these apparent advantages, the Na-Y NPs were synthesized via a bottom-up approach-a hydrothermal method utilizing silica and alumina as precursors, and tetramethylammonium bromide as an organic directing structured agent, all of which are expensive and not environmentally friendly. At the present time, a bottom-up approach to producing H-Y zeolite NPs using hydrothermal synthesis is not viable on a large scale. For this reason, a top-down approach using a ball milling (BM) technique and utilizing commercially available zeolite MPs is a promising alternative. BM offers a fast, simple, and environmentally friendly way of producing NPs. Recently, we reported optimizing the BM process to produce H-Y zeolite NPs using a high-energy ball mill [7,8]. Although optimized conditions for BM were established, the obtained product had low crystallinity. In this report, we attempted to improve the crystallinity of the H-Y zeolite NPs after BM using two separate methods: alkaline leaching and recrystallization.

2. Materials and methods

2.1 Raw materials

H-Y zeolite (CBV-720, Si/Al=15) was purchased from Zeolyst International and used as a parent sample. NaOH, Ludox AS-40 colloidal silica, and aluminum isopropoxide were purchased from Sigma Aldrich.

2.2 Ball milling

Wet BM of the zeolites was conducted using an Emax high energy ball mill (Retsch, Germany). Briefly, H-Y zeolite powder (5 g) was mixed with 30 mL of water and loaded into two jars (volume = 125 mL each) containing zirconia balls with diameters of 0.5 mm (total volume of balls was 75 mL/jar). The ball mill was connected to a Huber Unichiller (Huber, Germany) to prevent overheating. The ball mill was run for 30 min at 1000 rpm, as previously reported [7,8].

2.3 Alkaline leaching

After BM, the suspension was centrifuged at 5000 rpm for 10 min using a laboratory centrifuge. The top part of the solution, which contained NPs, was separated from the bottom part, which contained large flakes/slabs. Alkaline leaching was carried out by mixing 1 g of zeolite NPs after BM with 20 mL of 0.1 M NaOH solution in

a plastic bottle to form a suspension. The bottle containing the suspension was then put inside an oven set at 65ºC [9]. After 30 min, the bottle was removed from the oven, allowed to cool to room temperature, centrifuged, washed, and recentrifuged. The residue was allowed to dry in open air and then analyzed using XRD.

2.4 Recrystallization

Recrystallization was performed by mixing the zeolite NPs with a dilute aluminosilicate solution [10]. The dilute aluminosilicate solution was prepared by mixing 3.2397 g of NaOH, 0.7560 g of colloidal silica, 0.0408 g of aluminum isopropoxide, and 53.82 g of water in a plastic bottle, which was then heated at 90°C in an oven for 1 h to dissolve the solids and obtain a solution with a composition of $405Na_2O:1Al_2O_3:51SiO_2:29900H_2O$. After all the solids were dissolved, the zeolite NPs were added. After a certain period of time (10, 20, 60, and 90 min), the solid product was recovered using centrifugation and then characterized using XRD.

2.5 Characterization

Morphology of the samples were determined using an FEI Nova Nano scanning electron microscope (SEM) operating at a voltage of 5 kV. Phase crystallinity of the ball milled samples were determined using a Bruker D2 phaser desktop diffractometer. The diffractogram was scanned between 5 and 70º at a scan rate of 2º/min. Ball milled samples were also imaged using a Tecnai 200kV transmission electron microscope (TEM).

3. Results and discussion

SEM images showed that the parent H-Y zeolite MPs were irregular in shape, with a D50 of 550 nm (Figure 2A). After 30 min of BM, particle size was reduced to a D50 of 100 nm, while the crystallinity index decreased to 20% (Figure 2B). TEM images of the NPs revealed the presence of crystalline and non-crystalline phases (Figure 2C). Alkaline leaching was intended to remove the non-crystalline part of the NPs. SEM images of the NPs after the treatment showed further reduction in particle size (particle size <25 nm), implying possible removal of the non-crystalline phase, as intended (Figure 2D). The crystalline part of the NPs, however, was also affected, as shown in the diffractograms in Figure 3. As the leaching conditions were deemed too harsh, attempts were made to lower the concentration of the base and the temperature used. This, however, resulted in no significant difference—the H-Y zeolite NPs became amorphous after alkaline leaching. Desilication of the crystalline part of the H-Y NPs likely took place more easily when using a NaOH solution because a large external surface area was exposed after BM treatment. As a result, the alkaline leaching removed not only the amorphous silica phase, but also the crystalline phase. Alkaline leaching has been reported as an efficient method of preparing mesoporous zeolites, but it is often followed by a decrease in the crystallinity of the zeolites due to microporosity and loss of zeolitic hydroxyls [11].

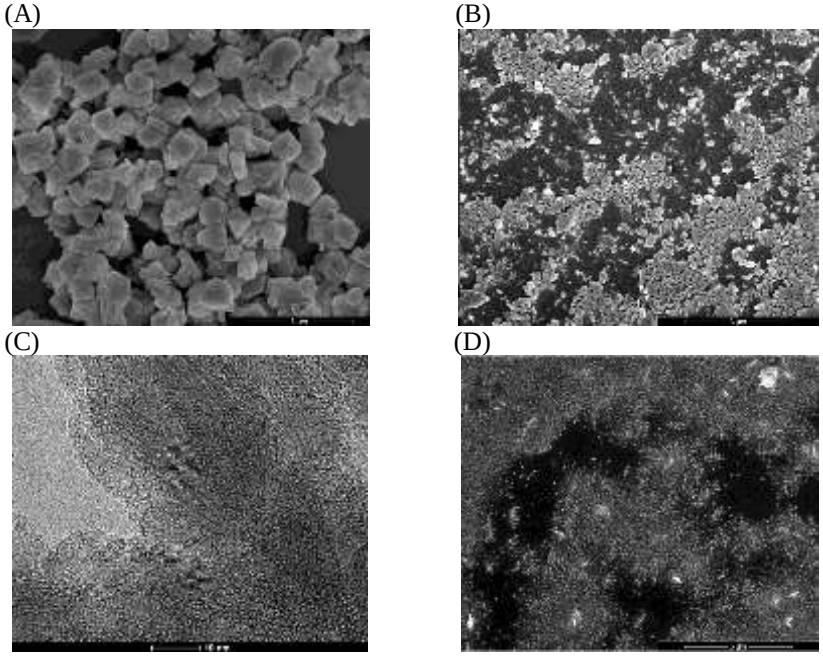

Figure 2 (A) Scanning electron microscope (SEM) images of parent H-Y zeolite microparticles; (B) SEM images of H-Y zeolite nanoparticles (NPs); (C) Transmission electron microscope images of H-Y zeolite NPs; and (D) SEM images of H-Y zeolite NPs after alkaline leaching.

In a separate approach, the H-Y zeolite NPs were subjected to heat treatment using a dilute aluminosilicate solution (recrystallization, see Figure 4). After only 10 min, the reflections caused by H-Y zeolites completely disappeared. This was not, however, compensated for by the formation of broad reflection between 15 and 30º synonymous with an amorphous silica phase, as seen for the alkaline leached samples; the diffractogram was rather flat. Increasing the recrystallization time to 20 min produced several minor reflections that became more apparent following longer treatment. The reflection pattern was different, however, from that of the parent sample before the recrystallization-after recrystallization, zeolite reflections matched the pattern for an SOD framework, rather than the FAU type.

In this preliminary study, alkaline leaching was unable to increase the crystallinity of H-Y zeolite NPs post-BM, despite this method having been reported as being successful in recovering the crystallinity of H-ZSM-22 (framework type TON) after BM [9]. The differences could be related to topology, as previous reports have shown that topology indeed affects desilication [12-14]. Because lowering the concentration of the base and the temperature showed no effect, further studies will focus on lowering the treatment time (<30 min). Unlike alkaline leaching, recrystallization was intended to heal the non-crystalline phase. The recrystallization method used was adapted from an earlier study regarding preparing nano zeolite X [4]. Given that zeolite Y and X bear a similar framework type (FAU), differing only in their Si/Al ratios (Si/Al = 1 in zeolite X, Si/Al = 15 in the zeolite Y we used), we expected similar outputs. Our preliminary results, however, were rather unexpected. Although the process did increase the crystallinity, it simultaneously transformed the FAU framework to an SOD framework. We hypothesize that this is possibly related to the composition of the dilute aluminosilicate solution used, and further studies will focus on varying the solution composition. Although the formation of an SOD-type framework was not desired, the transformation of an FAU into an SOD framework during recrystallization is interesting, given that an FAU-type framework (X/Y) contains both *sod* and *d6r* CBUs, whereas the SOD framework contains only *sod* CBUs (llustrated in Figure 1). The evolution of the diffractogram pattern suggests that the *sod* CBUs in the H-Y zeolites may not be completely destroyed during BM at the initial stage of recrystallization (unlike the *d6r*) and that prolonged recrystallization rearranges the *sod* CBUs to form an SOD framework.

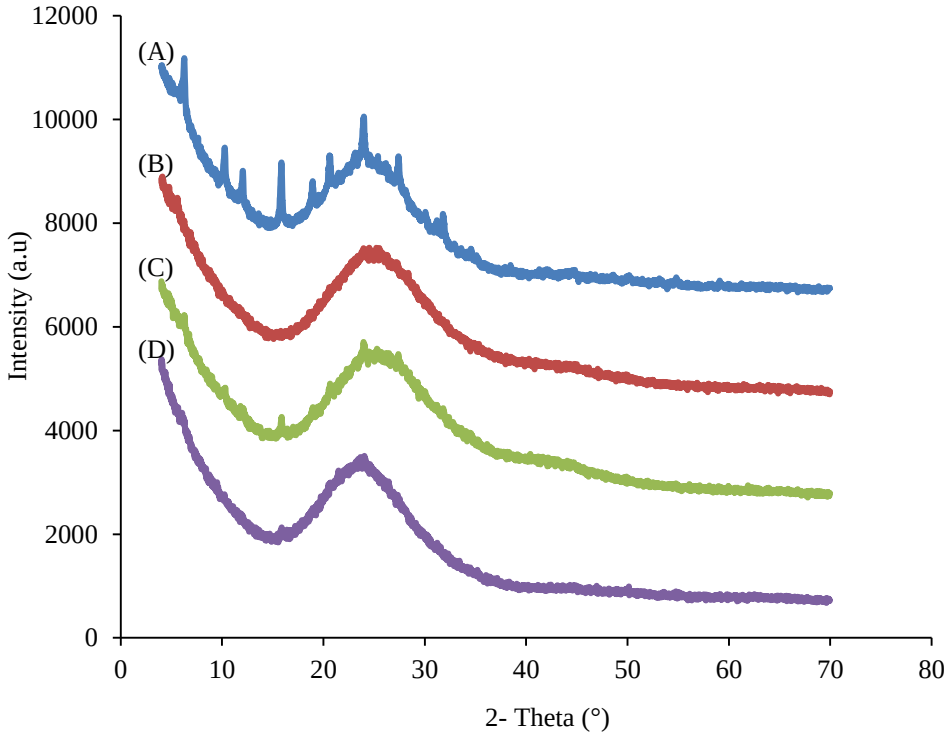

Figure 3 X-ray diffractogram of H-Y zeolite nanoparticles (A) before and after alkaline leaching for 30 min using (B) 0.1M NaOH at 65ºC, (C) 0.05M NaOH at 65ºC, and (D) 0.05M NaOH at 25ºC.

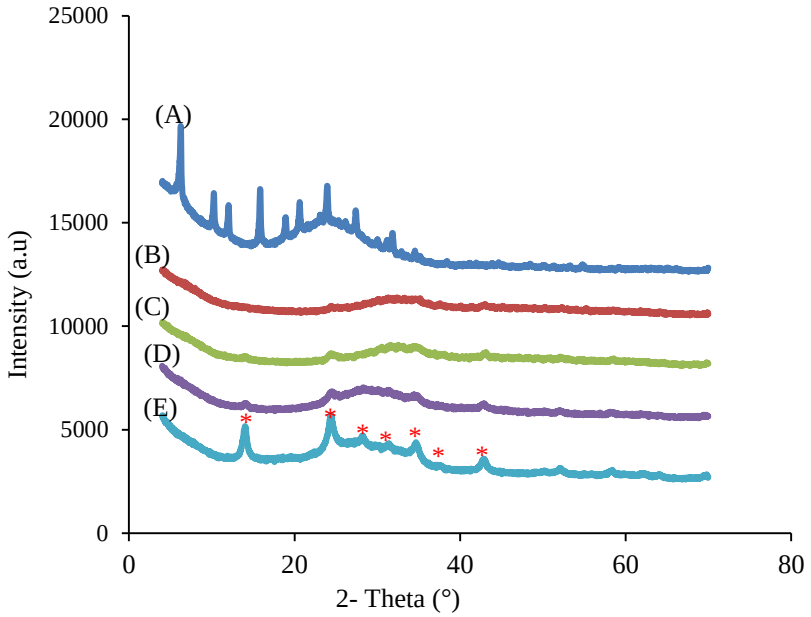

Figure 4 X-ray diffractogram of H-Y zeolite nanoparticles (A) before and after recrystallization for (B) 10, (C) 20, (D) 60, and (E) 90 min. All reflections in (A), except the broadband at 15 - 30º, match the reflections expected from a faujasite-type framework. Red asterisks are reflections due to a sodalite-type framework.

A literature survey of methods combining BM with recrystallization to produce hierarchical and zeolite NPs is summarized in Table 1. Anand et al. [15] used an in-situ BM and recrystallization technique to produce Na-A zeolite (LTA-type framework) NPs using a specialized milling apparatus capable of handling high alkalinity and temperature. Three events-miniaturization, amorphization, and recrystallization-took place in a one-pot process. Kurniawan et al. [16] used a sequential combination of BM and recrystallization to produce mordenite zeolites (MOR-type framework). The combination was performed without additional alkaline leaching prior to recrystallization and the crystalline phase after BM acted as seeds for the formation of mordenite NPs. Although particle size increased after recrystallization, the particles were still within the nanometer size range. It was suggested that the mechanical treatment did not destroy the zeolite framework but distorted the T-O-T angles, making it easier for the seeds to grow and recrystallize following the initial frameworks. In contrast, during alkaline leaching in the current work, the T-O-T bonds of H-Y zeolite were likely broken, which may have later promoted inter-zeolite conversion during recrystallization. The combination of sequential BM and recrystallization has also been reported to produce hierarchical ZSM-5 (MFI-type framework) NPs [17]. The growth of the NPs during recrystallization after BM was prevented by adding cetyltrimethylammonium bromide (CTABr) to the alkaline solution. The authors reported that the CTABr prevented excessive coalescence and crystal growth, and assembled the nano-sized zeolites; without the CTABr, recrystallization produced micron-sized ZSM-5 crystals.

Miyagawa et.al [18] used a dry BM technique with KOH and a FAU-type zeolite, and then heat treated the resulting powder using a small amount of steam. They found that the FAU-type framework interconverted into a CHA-type framework. They reported that the additive amount of KOH is a key factor for the interzeolite transformation of FAU-type zeolite into CHA-type zeolite without the use of solvent and OSDA. Interconversion was also reported for Na-Y zeolite (FAU) into ZSM-5 (MFI) without following the BM process and instead using only a heat treatment with a suitable alkaline and silica ratio [19]. In the current work, the H-Y zeolite was converted into sodalite using a recrystallization solution of 405 Na_2O:1Al_2O_3:51 SiO_2:29900 H_2O. The FAU framework is possibly able to be converted to other zeolite frameworks by tuning the composition of the recrystallization solution. The BM led to a large external surface area of H-Y zeolite, which makes it easier for NaOH to destroy the crystalline phase. As a result, interzeolite conversion occurred during the heat treatment.

Table 1 Comparison of reported methods combining ball milling (BM) and recrystallization to produce zeolite nanoparticles (NPs) and hierarchical zeolites.

No	Initial zeolite (Framework)	BM conditions	Recrystallization conditions	Final zeolite (Framework)	Ref.
1	H-Y (FAU)	1000 rpm	405 Na_2O:1 Al_2O_3:51 SiO_2:29900 H_2O	Sodalite (SOD)	Current work
2	Na-A (LTA)	3000 rpm (50 g Na-A:500 mL 2M NaOH)	BM and recrystallization combination was performed in situ.	Na-A (LTA) NPs	[15]
3	Mordenite (MOR)	3000 rpm	12 NaOH:18 SiO_2:780 H_2O	Mordenite (MOR) NPs	[16]
4	ZSM-5 (MFI)	500 rpm	1 SiO_2:0.89 NaOH:56.49 H_2O:x CTABr	ZSM-5 (MFI) hierarchical	[17]
5	Na-Y (FAU)	150 rpm, dry BM of zeolite and KOH	Heat treatment at 120°C for 3 – 48 h using a small amount of water as steam.	Chabazite (CHA)	[18]
6	Na-Y, H-Y (FAU)	No BM	$NaOH/SiO_2$	ZSM-5 (MFI)	[19]

4. Conclusion

A preliminary study using two different approaches, alkaline leaching and recrystallization, was carried out with the intention of improving the crystallinity of H-Y zeolite NPs after BM. Alkaline leaching reduced the size of the NPs significantly, but did not improve their crystallinity. Instead, the treatment turned NPs into a completely amorphous phase that could not be significantly ameliorated by decreasing the base concentration or leaching temperature. In contrast, recrystallization of the NPs using a dilute aluminosilicate solution initially turned the H-Y zeolite NPs into an amorphous phase, followed by conversion to an SOD-type crystalline framework.

5. Acknowledgements

S and RH thank ADNOC Refining Research Center (ARRC) for funding. S thanks ITB for P3MI 2020 funding. The authors thank Dr. Abdullah Khalil of NYU-Abu Dhabi for taking the TEM image of the BM H-Y NPs.

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